Eur. Phys. J. B **19**, 17–20 (2001)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Variational calculations of ionized-donor-bound excitons in GaAs-$Al_xGa_{1-x}As$ quantum wells*

J.J. Liu[1,2,a], S.F. Zhang[1], Y.X. Li[1,2], and X.J. Kong[1,2]

[1] Department of Physics, Hebei Normal University, Shijiazhuang 050016, PR China
[2] National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Science, Beijing 100083, PR China

Received 17 July 2000 and Received in final form 13 November 2000

Abstract. Using a two-parameter wave function, we calculate variationally the binding energy of an exciton bound to an ionized donor impurity (D^+, X) in GaAs-$Al_xGa_{1-x}As$ quantum wells for the values of the well width from 10 to 300 Å, when the dopant is located in the center of the well and at the edge of the well. The theoretical results confirm that the previous experimental speculation proposed by Reynolds *et al.* [Phys. Rev. B **40**, 6210 (1989)] is the binding energy of D^+, X for the dopant at the edge of the well. In addition, we also calculate the center-of-mass wave function of the exciton and the average interparticle distances. The results are discussed in detail.

PACS. 71.35.-y Excitons and related phenomena – 73.20.Dx Electron states in low-dimensional structures (superlattices, quantum well structures and multilayers)

1 Introduction

For years, there has been a great deal of interest in bound excitons (BE) states in bulk semiconductors [1,2]. The BE states have been observed in many semiconductors since the early 1960s. They are very common because most practical semiconductors containing impurities or defects in significant quantity can produce this binding. The binding energy of the exciton to the impurity or defect is generally weak, compared to the free-exciton binding energy. The recent advances in the crystal growth technique of molecular epitaxy allow the engineering of semiconductors on an atomic scale such as superlattices or quantum wells (QWs) [3]. In these heterostructures, the quantum confinement effects may become important. Particularly the Coulomb interaction between electrons and holes is increased because the wave function is compressed along the growth-axis. Therefore excitonic effects become more important than those in the bulk semiconductors and excitons may be observed up to room temperature because the thermal ionization is less efficient [4,5]. The original report of donor-related complexes in quantum wells was first proposed by Shanabrook and Comas [6]. Liu *et al.* [7] observed transitions in the photoluminescence associated with excitons bound to neutral and ionized donors (D^+, X) located at the center of the well (CW). Up to now, we have known that the two-dimensional (2D) D^+, X energies [8] are about four times greater than those obtained in the three-dimensional (3D) case [9]. The energies in the QWs are expected to be between the 2D and 3D limits. There has been some experimental data about D^+, X states in GaAs-$Al_xGa_{1-x}As$ QWs, but few theoretical studies concerning it except for reference [10]. The speculative binding energies of D^+, X associated with donors at the center of the barrier and/or edge of the well (EW) in reference [11] remain unconfirmed. So, it is necessary to make further theoretical study for the D^+, X complex in QWs.

In this paper, using the two-parameter wave function, we calculate variationally the binding energy of a heavy-hole exciton bound to an ionized donor impurity located in CW and EW. For the dopant at EW, we discuss and compare our results with experimental data [11], and determine the speculation in reference [11]. Besides, we calculate the center-of-mass wave function of the exciton and the average interparticle distances for the dopant in CW, which play an important role in studying the properties of D^+, X in QWs.

2 Theory

Here we suppose that the band offsets are weak enough so that the effective-mass approximation may be used. Then the Hamiltonian of D^+, X in the single quantum wells

* The project supported by the National Natural Science Foundation of China under Grant No. 69736010, and the Hebei Natural Science Foundation under Grant No. 199181.

[a] e-mail: liujj@hebtu.edu.cn

(SQWs) can be written as

$$H = -c_{\rm e}\nabla_{\rm e}^2 - c_{\rm h}\nabla_{\rm h}^2 - \frac{2}{\sqrt{\rho_{\rm e}^2+(z_{\rm e}-z_0)^2}} + \frac{2}{\sqrt{\rho_{\rm h}^2+(z_{\rm h}-z_0)^2}} - \frac{2}{\sqrt{\rho_{\rm eh}^2+(z_{\rm e}-z_{\rm h})^2}} + V_{\rm e} + V_{\rm h}, \quad (1)$$

where subscript e is the electron and h the hole, z_i is the relative coordinate to the origin along the layer normal (001) direction, $\boldsymbol{\rho}_i$ is the relative coordinate to the origin in 2D plane ($i = {\rm e}, {\rm h}$), $\rho_{\rm eh}$ is the distance between the electron and the hole in 2D plane, $(0, 0, z_0)$ is the dopant position, $c_{\rm e} = m_{\rm ew}/m_{\rm e}$, $c_{\rm h} = m_{\rm ew}/m_{\rm h}$, $m_{\rm ew}$ is the effective mass of conduction electron in GaAs, $m_{\rm e}$ ($m_{\rm h}$) is the effective mass of the conduction electron (the heavy hole) in GaAs or $Al_xGa_{1-x}As$. The potential wells for the conduction electron $V_{\rm e}$ and for the heavy hole $V_{\rm h}$ are assumed to be square wells of width d. Here we have chosen, without any loss of generality, the origin of the coordinate system to be the center of the GaAs well. The values of the potential well heights $V_{\rm e}$ and $V_{\rm h}$ are determined from the Al concentration in $Al_xGa_{1-x}As$.

In our calculations, the units of distance and energy are the Bohr radius and electron Rydberg in GaAs, respectively; $a_{\rm B} = \epsilon_{\rm w}\hbar^2/e^2m_{\rm ew}$, $R_y = e^2/2\epsilon_{\rm w}a_{\rm B}$, where $\epsilon_{\rm w}$ is the dielectric constant in GaAs.

For the D^+, X system we use the wave function [12–14]

$$\Psi = \Phi(\boldsymbol{\rho}_{\rm e}, \boldsymbol{\rho}_{\rm h}) f_{\rm e}(z_{\rm e}) f_{\rm h}(z_{\rm h}), \quad (2)$$

where $f_{\rm e}(z)$ and $f_{\rm h}(z)$ are taken to be ground state solutions of an electron and a hole for the finite square well potentials, respectively. To simplify the calculation we have not included an explicit z dependence in Φ. The Hamiltonian of interest is then just $H_{\rm eff}$, which can be written in dimensionless form:

$$H_{\rm eff} = -c_{\rm e}\nabla_{\rm e}^2 - c_{\rm h}\nabla_{\rm h}^2 - 2(U_{ed} - U_{{\rm h}d} + U_{\rm eh}), \quad (3)$$

where $c_{\rm e} = m_{\rm ew}/m_{{\rm e}\|}$, $c_{\rm h} = m_{\rm ew}/m_{{\rm h}\|}$, $m_{{\rm e}\|}$ ($m_{{\rm h}\|}$) is the effective 2D mass of the electron (the heavy hole), as can be calculated from reference [15]. U_{ed}, $U_{{\rm h}d}$, and $U_{\rm eh}$ come from the effective 2D Coulomb interaction. U_{ed}, $U_{{\rm h}d}$ are defined by [12–14]

$$U_d(\rho) = \int \frac{f_{\rm e}^2(z_{\rm e})}{\sqrt{\rho_{\rm e}^2+(z_{\rm e}-z_0)^2}} {\rm d}z_{\rm e} = \frac{1-{\rm e}^{-\gamma_d\rho_{\rm e}}}{\rho_{\rm e}}, \quad (4)$$

and $U_{\rm eh}$ is defined by

$$U_{\rm eh}(\rho) = \int\int \frac{f_{\rm e}^2(z_{\rm e}) f_{\rm h}^2(z_{\rm h})}{\sqrt{\rho^2+z^2}} {\rm d}z_{\rm e}{\rm d}z_h = \frac{1-{\rm e}^{-\gamma_x\rho}}{\rho}, \quad (5)$$

where $z = z_{\rm e} - z_{\rm h}$, $\boldsymbol{\rho} = \boldsymbol{\rho}_{\rm e} - \boldsymbol{\rho}_{\rm h}$ is the relative coordinate in 2D plane, γ_d^{-1}, γ_x^{-1} is a measure of the well width $d/a_{\rm B}$. In equation (4), we have chosen $\gamma_{ed} = \gamma_{{\rm h}d} = \gamma_d$. These approximations were justified in reference [14]. The parameter γ_d must be calibrated by requiring that equation (4) gives the correct binding energy for the impurity state in SQWs. As to the details, see reference [13] and [14]. A similar calculation is made for the exciton state in SQWs, from which the γ_x is obtained [13,14].

To solve the problem of the bound states of the effective 2D D^+, X system, we have to find the wave function Φ in equation (2) satisfying the wave equation

$$H_{\rm eff}\Phi = E\Phi. \quad (6)$$

We restrict our study to the ground state, corresponding to the lowest energy value E, which is determined by means of variational calculations. Here we use a wave function in the effective 2D D^+, X system, which has a similar form to that in the calculation of Liu *et al.* [13,14,17,18], *i.e.*,

$$\Phi(\boldsymbol{\rho}_{\rm e}, \boldsymbol{\rho}_{\rm h}) = N\phi_{\rm c}(\mathbf{R}_{\rm eh})\phi_x(\boldsymbol{\rho}_{\rm eh}), \quad (7)$$

where N is the normalization constant, $\phi_x(\boldsymbol{\rho}) = {\rm e}^{-\alpha_x\rho}$ is Slater $1s$ orbitals describing the effective 2D exciton, and $\phi_{\rm c}(\mathbf{R})$ is a wave function describing the center-of-mass motion of the effective 2D exciton. $\mathbf{R}_{\rm eh} = (m_{{\rm e}\|}\boldsymbol{\rho}_{\rm e} + m_{{\rm h}\|}\boldsymbol{\rho}_{\rm h})/(m_{{\rm e}\|} + m_{{\rm h}\|}) = (\sigma\boldsymbol{\rho}_{\rm e} + \boldsymbol{\rho}_{\rm h})/(1+\sigma)$ is the center-of-mass coordinate for the effective 2D exciton, and $\boldsymbol{\rho}_{\rm eh} = \boldsymbol{\rho}_{\rm e} - \boldsymbol{\rho}_{\rm h}$ is the relative coordinate of electron and hole in the effective 2D exciton. The energy of the D^+, X system is

$$E = \frac{\int \Phi^* H_{\rm eff}\Phi {\rm d}\tau}{\int |\Phi|^2 {\rm d}\tau}, \quad (8)$$

where ${\rm d}\tau = {\rm d}^2\boldsymbol{\rho}_{\rm e}{\rm d}^2\boldsymbol{\rho}_{\rm h}$ is the total volume element. We assume $\phi_{\rm c}(\mathbf{R}) = R^\alpha {\rm e}^{-\beta R}$, where α and β are the nonlinear variational parameters which are adjusted to minimize the energy E of the bound exciton system. In our calculations, we use the varying values for the conduction-band and valence-band mass parameters and the dielectric constants in GaAs and $Al_{0.3}Ga_{0.7}As$. The material parameters used in the calculation are listed in Table 1. Using the values of α_x, γ_d, γ_x, obtained previously, we obtain the binding energy of D^+, X:

$$E_{dx{\rm b}} = E - E_{x{\rm b}}, \quad (9)$$

where $E_{x{\rm b}}$ is the binding energy of the $1s$ exciton state in SQWs. The $E_{dx{\rm b}}$ *versus* the well width is shown in Figure 1. With the two variational parameters α and β, we can also obtain the center-of-mass wave function of the exciton

$$\phi_{\rm c}(\mathbf{R}) = AR^\alpha {\rm e}^{-\beta R}, \quad (10)$$

where A is the normalization constant. The $\phi_{\rm c}(\mathbf{R})$ *versus* the radius R is shown in Figure 2. And the average interparticle distances can be obtained by

$$\langle r\rangle = \frac{\int \Phi^* r\Phi {\rm d}\tau}{\int |\Phi|^2 {\rm d}\tau}, \quad (11)$$

the $\langle r\rangle$ *versus* the well width is shown in Figure 3.

Table 1. Material parameters of GaAs and $Al_{0.3}Ga_{0.7}As$ used in the calculation.

Material	ΔE_g(meV)	$\Delta E_c/\Delta E_g$	γ_1	γ_2	m_e^*	ϵ
GaAs[a]			6.85	2.1	0.0665	12.5
	379.80[b]	57%[a]				
$Al_{0.3}Ga_{0.7}As$			5.22[c]	1.40[c]	0.0914[d]	11.8[d]

[a] Ref. [10]. [b] Ref. [16]. [c] Ref. [19]. [d] Ref. [20].

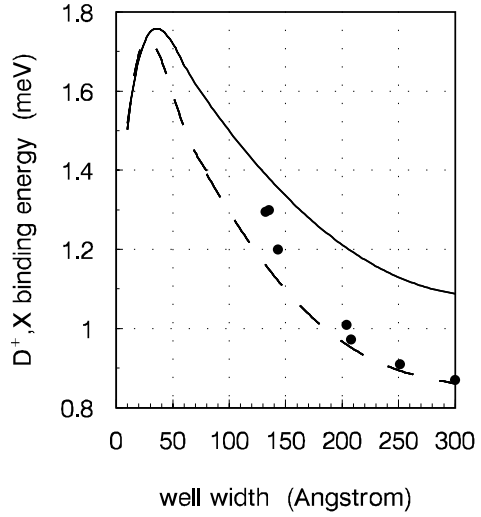

Fig. 1. Binding energy $E_{dx\mathrm{b}}$ of an exciton bound to an ionized donor located at CW and EW as a function of well thickness. The solid curve is the result of CW, the dashed curve is the result of EW and the circles are the experimental points of reference [11].

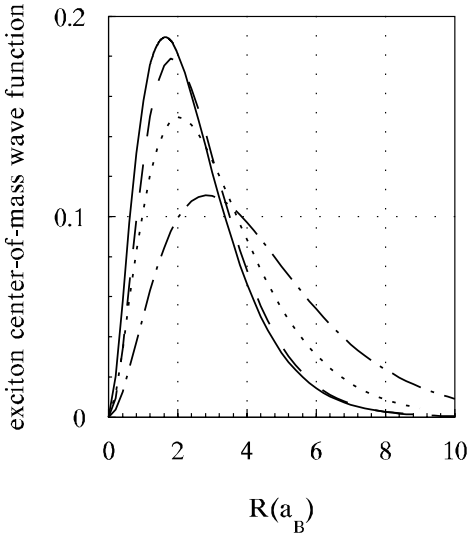

Fig. 2. The center-of-mass wave functions of the exciton as functions of the effective 2D radial distance R for the various well widths when the dopant is located in CW. The dashed curve is the result of the well width of 10 Å, the solid curve is the result of the well width of 30 Å, the dotted curve is the result of the well width of 100 Å, the dot-dashed curve is the result of the well width of 300 Å.

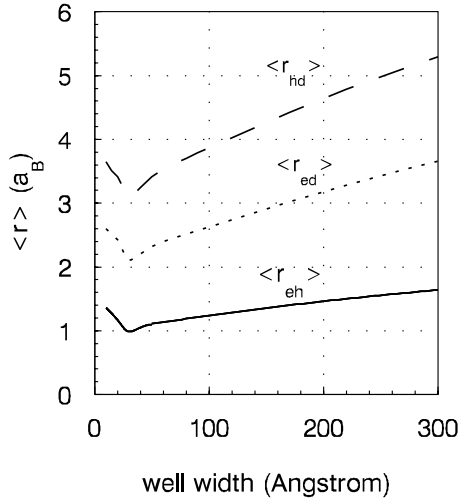

Fig. 3. The average interparticle distances as functions of well thickness for the dopant in CW.

3 Results and discussion

1. The binding energy of D^+, X when the dopant is located in CW: We calculate the binding energy of D^+, X as a function of the well size from 10 to 300 Å, and find the binding energy increases as the well size is increased to about 30 Å, after which the binding energy decreases. It can be seen from Figure 1 that the binding energy of D^+, X appears a peak value of 1.742 meV, which is an inevitable outcome for SQWs with finite potential barrier. The position of the binding energy peak appears at around 30 Å, which is less than 50 Å in the previous work [10] because of concerning the effect of effective mass and dielectric constant mismatch in the two materials. This is also the position of the peak for the exciton states. It is easy to understand, since the electron and hole are bound by the same potentials both in the case of D^+, X and of exciton states.

In the two limits where the well width becomes infinity or zero, our wave function (2) becomes questionable because of the separation of the coordinates. In the wider well, the exciton radius is far less than the well width (Fig. 3), so the system tends to 3D case [9]. In this case our wave function (2) is not well adapted, which cause a underestimation of the binding energy for large wells. In the other side of narrower well, the mass discontinuity inhibits tunneling and thus raises the binding energy. As to the well size down to about 10 Å, the mass discontinuity

almost vanishes, and the effective mass tends to recover the 3D case.

The two-parameter wave function (7) we used has a clear physical idea and a simple mathematical form, and incorporates important interparticle correlation effects.

When we calculate the binding energy of D^+, X system, only the two variational parameters in the wave function are determined by minimizing the value E of the total energy of the bound exciton. Our results have been obtained without adopting any adjustable parameters in our theory. So the two-parameters wave function we chose can describe the properties of D^+, X system.

2. The binding energy of D^+, X when the dopant is located at EW: When the dopant is located at EW, the binding energy of D^+, X has a peak too. Its position is similar to that of the dopant in CW. The peak value is about 1.720 meV. The binding energy of EW (D^+, X) is smaller than that of CW (D^+, X), and the gap value increases as the well size is increased. These properties result from the fact that the repulsive barrier potential tends to push the particle charge distribution away from the attractive ionized center thereby leading to a reduced effective Coulomb attraction. The wider the well is, the less tightly bound the EW system is than the CW system; and the more the EW wave function spread into the barrier, the smaller the binding energies are.

By comparing the experimental data in reference [11] with our results, we can see from Figure 1 that the experimental data in reference [11] agrees fairly with the result of the dopant at EW. As is known to all, the system binding energy for the dopant in barrier is smaller than that for the dopant at EW. So, we can determine the speculation in reference [11] is the binding energy of D^+, X for the dopant at EW.

3. The center-of-mass wave function of the exciton for the dopant in CW: It can be seen from Figure 2 that the center-of-mass wave function of the exciton is centered very close to the origin and spreads out in coordinate space. At the well width of about 30 Å, the $\phi_{\rm c}(\mathbf{R})$ reaches the most centralized distribution, and at the other well widths, the $\phi_{\rm c}(\mathbf{R})$ spreads out gradually, particularly at the wider well, which agrees reasonably with the changing tendency of the binding energy for the various well widths. Therefore the average interparticle distances have a minimum value at the well width of about 30 Å, after which they yield an increase as the well size is increased, as we can see from Figure 3 apparently.

4. The average interparticle distances of D^+, X for the dopant in CW: It can be seen from Figure 3 that the average interparticle distances yield reductions as the well size is increased to about 30 Å, after which they increase. The changing tendency of the average interparticle distances is reverse to that of the binding energy. When the well width is about 30 Å, the average interparticle distances take their smallest values while the $E_{dx\rm b}$ takes its greatest value, and the $E_{dx\rm b}$ yields a reduction as the average interparticle distances are increased. The average distance of donor-electron is smaller than that of donor-hole, which is due to the Coulomb potential. The distance of electron-hole varies little with the well width leading to the system tends to 3D case for large well, as is discussed above. All of these properties are reasonable.

The center-of-mass wave function of the exciton and the average interparticle distances for the dopant at EW are similar to those for the dopant in CW.

In conclusion, we have calculated the binding energy of D^+, X in GaAs-$Al_{0.3}Ga_{0.7}As$ SQWs for the dopant in CW and at EW, the center-of- mass wave function of the exciton and the average interparticle distances for the dopant in CW as a function of the well size from 10 to 300 Å. The results yielded an increase in binding energy as the well size is increased to about 30 Å, after which the binding energy decreases. The center-of-mass wave function reaches the most centralized distribution and the average interparticle distances reach the smallest value at the well size of about 30 Å. Their changing tendencies for the various well widths are consistent theoretically. By comparing our results with the experimental data, we have determined the speculation in reference [11] is the binding energy of D^+, X for the dopant at EW.

References

1. P.J. Dean, D.C. Herbert, in *Excitons of Topics in Current Physics*, edited by K. Cho (Springer Verlag, Berlin, 1979), Vol. 14, p. 55.
2. D.C. Reynolds, T.C. Collins, *Excitons: Their Properties and Uses* (Academic Press, New York, 1981), p. 110.
3. L. Esaki, in *Physics and Applications of Quantum Wells and Superlattices*, edited by E.E. Mendez, K. von Kilitzing, NATO ASI Series, Series B: Physics, Vol. 170 (Plenum Press, New York, 1987), p. 1.
4. R.C. Miller, D.A. Kleinman, W.T. Tsang, A.C. Gossard, Phys. Rev. B **24**, 1134 (1981).
5. G. Bastard, E.E. Mendez, L.L. Chang, L. Esaki, Phys. Rev. B **26**, 1974 (1982).
6. B.V. Shanabrook, J. Comas, Surf. Sci. **142**, 504 (1984).
7. X. Liu, A. Petrou, B.D. Mecombe, J. Ralston, G. Wicks, Phys. Rev. B **38**, 8522 (1988).
8. L. Stauffer, B. Stebe, Phys. Rev. B **39**, 5345 (1989).
9. L. Stauffer, B. Stebe, G. Munschy, Phys. Stat. Sol. (b) **119**, 193 (1983).
10. L. Stauffer, B. Stebe, Solid State Comm. **80**, 983 (1991).
11. D.C. Reynolds, C.E. Leak, K.K. Bajaj, C.E. Stutz, R.L. Jones, Phys. Rev. B **40**, 6210 (1989).
12. D.A. Kleinman, Phys. Rev. B **28**, 871 (1983).
13. J.J. Liu, X.J. Kong, Phys. Rev. B **55**, 1349 (1997).
14. J.J. Liu, X.J. Kong, Y. Liu, J. Appl. Phys. **84**, 2638 (1998).
15. C. Prister, G. Allan, M. Lannoo, Phys. Rev. B **30**, 7302 (1984).
16. R.L. Greene, K.K. Bajaj, Solid State Comm. **45**, 825 (1982).
17. J.-J. Liu, X.J. Kong, C.W. Wei, S.S. Li, Chin. Phys. Lett. **15**, 588 (1998).
18. J.J. Liu, Y.X. Li, X.J. Kong, S.S. Li, Chin. Phys. Lett. **16**, 526 (1999).
19. The Kohn-Luttinger parameters are obtained by linearly interpolation between the values given in reference [13].
20. C. Mailhiot, Y.C. Chang, T.C. Megill, Phys. Rev. B **26**, 4449 (1982).